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16. ABSTRACT

Coarse particles (2.5 to 10 μm) were collected in dichotomous samplers and analyzed by scanning electron microscopy and x-ray fluorescence. The resulting data were used in a chemical mass balance receptor model, and the mass concentration of coarse particles was apportioned into 8 components, which included 2% coal fly ash and 25% botanical matter. Mineral concentrations deduced by electron microscopy were in good agreement with soil deduced from bulk compositional data. A comparison of results for an incinerator component indicated possible biases in results by both methods.

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USE OF ELECTRON MICROSCOPY DATA IN RECEPTOR MODELS FOR PM-10

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Abstract—Coarse particles (2.5–10 μm) were collected in dichotomous samplers and analyzed by scanning electron microscopy. The resulting data for coal-fly ash and botanical matter were included with x-ray fluorescence and neutron activation data in a chemical mass balance receptor model for fine and coarse particles, and the mass concentration of particles with diameters $< 10\,\mu$m was apportioned into 10 components. Mineral concentrations deduced by electron microscopy were in good agreement with soil concentrations deduced from x-ray fluorescence data. A comparison of results for an incinerator component indicated possible biases in results.

Key word index: Coal fly ash, coarse particles, electron microscopy, fine particles, fly ash, incinerator, minerals, PM-10, receptor models, spores.

INTRODUCTION

Receptor models, along with dispersion models, may be used in polluted areas of the U.S. to develop plans to meet the new national air quality standard for particles with diameters $< 10\,\mu$m (PM-10) (EPA, 1987). A receptor method that is a composite of multiple linear regression and chemical mass balance (CMB) models was applied to aerosol data from Philadelphia, PA and Camden, NJ, and PM-10 was resolved into several components (Dzubay *et al.*, 1988; Dzubay, 1988). One component was crustal matter, which included unresolved amounts of soil and coal-fly ash.

A scanning electron microscope (SEM) with an energy dispersive x-ray detector (EDX) can distinguish individual coal-fly ash particles from soil minerals by morphology. In studies conducted in Philadelphia over 95% of coal-fly ash particles with diameters $< 10\,\mu$m appeared as smooth spheres whereas soil minerals were irregular or crystal shaped (Mamane *et al.*, 1986; Mamane and Dzubay, 1988). Furthermore, mass concentration for each particle type can be deduced by estimating particle volume from SEM data and assuming a value for density. Here we explore the feasibility of increasing the resolution of the CMB method by using SEM-EDX data with x-ray fluorescence (XRF) data.

In the Philadelphia study, aerosol samples were collected on Teflon filters in dichotomous samplers at three sites shown in Fig. 1 and analyzed for bulk elemental composition (Dzubay *et al.*, 1988). Additional samples were collected simultaneously on Nuclepore filters in dichotomous samplers at two of the sites. Here we describe SEM-EDX analyses of coarse particles (2.5–10 μm aerodynamic diameter) and present estimates of mass concentrations of minerals, coal-fly ash, botanical matter and incinerator emissions. We show how the SEM-EDX data for botanical matter and coal-fly ash can be included in CMB calculations. We compare SEM-EDX and CMB results for incinerator emissions and discuss possible biases for both methods.

Small spacing among fine particles ($< 2.5\,\mu$m) collected in dichotomous samplers prevented them from being analyzed reliably by SEM. Elsewhere we describe a modified dichotomous sampler that collects both fine and coarse particles suitable for analysis by XRF and SEM (Mamane and Dzubay, 1989).

EXPERIMENTAL PROCEDURE

Aerosol samples were collected on 0.3-μm pore size Nuclepore filters in Beckman automated dichotomous samplers at sites 12 and 28 (See Fig. 1) between 14 July and 13 August 1982. Each sampler had a PM-10 inlet that was a prototype of Sierra-Andersen model SA 246 inlet. The flow rate through each inlet was 16.7 $\ell\,\text{min}^{-1}$. Filters were changed twice daily at 0600 and 1800 EDT. Additional samples were collected simultaneously on Teflon filters in collocated dichotomous samplers. Coarse fraction Teflon and Nuclepore filters were coated with 25 $\mu\text{g}\,\text{cm}^{-2}$ of mineral oil before sampling (and before tare weight determinations) to improve adhesion of

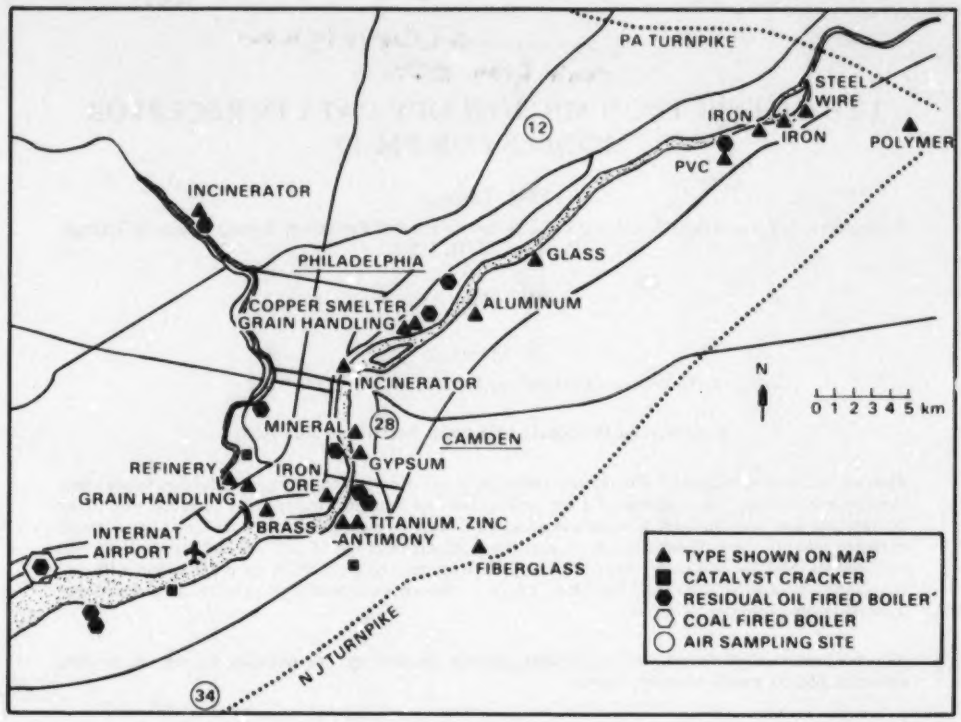

Fig. 1. Map of Philadelphia environs showing sampling sites and emission sources.

large particles. All filters were analyzed for element and mass concentrations by XRF and beta gauge, and fine Teflon filters were analyzed for element concentrations by instrumental neutron activation analysis (INAA) (Dzubay *et al.*, 1988).

Individual coarse particles on Nuclepore filters were analyzed by SEM-EDX for 12 sampling periods. Periods were not selected randomly but were selected to provide a variety of cases of high and low concentrations of incinerator particles. A 4-mm by 4-mm piece of each Nuclepore filter was coated under vacuum with a thin carbon layer and analyzed in an Amray Model 1000 SEM. Analysis conditions were 30-keV electron energy, 100-μA beam current, 26° sample tilt and 12-mm working distance. For each sample, all particles larger than 1.5 μm were analyzed manually in five to ten randomly chosen fields. About 200–300 particles were analyzed per sample. For each particle, two perpendicular diameters were recorded, morphological characteristics were noted and an x-ray spectrum was obtained for 30-to 60-s counting time.

RESULTS AND DISCUSSION

Scanning electron microscopy results

Criteria shown in Table 1 were used to classify coarse particles into the following categories: mineral, coal-fly ash, botanical and incinerator emissions. To

Table 1. Criteria for classifying particles into categories

Category	Density (g cm^{-3})	Morphology	Major x-ray peaks
Mineral	2.6 ± 0.3	Nonspherical	High peak to background ratio for Si or Ca and variable amounts of Al, K, Ti and Fe
Coal-fly ash	2.6 ± 0.3	Smooth sphere	Same as mineral
Botanical	1.3 ± 0.2*	Characteristic of spores or pollen†	Low peak to background ratio for variable amounts of P, S, K, and Ca
Incinerator	2.6 ± 0.3‡	Non-specific	Spectrum for mineral elements§ or carbon‡ with Cl, K and Zn
Sea salt	2.2 ± 0.2	Non-specific	Mainly Cl with detectable Na

* Density of spores from Sussman and Halvorson (1966).
† Morphologies for many spores and pollens are illustrated by Kapp (1969).
‡ For the few carbonaceous incinerator particles, a density of 1 g cm^{-3} was assumed.
§ X-ray spectra for incinerator particles are shown by Mamane (1988).

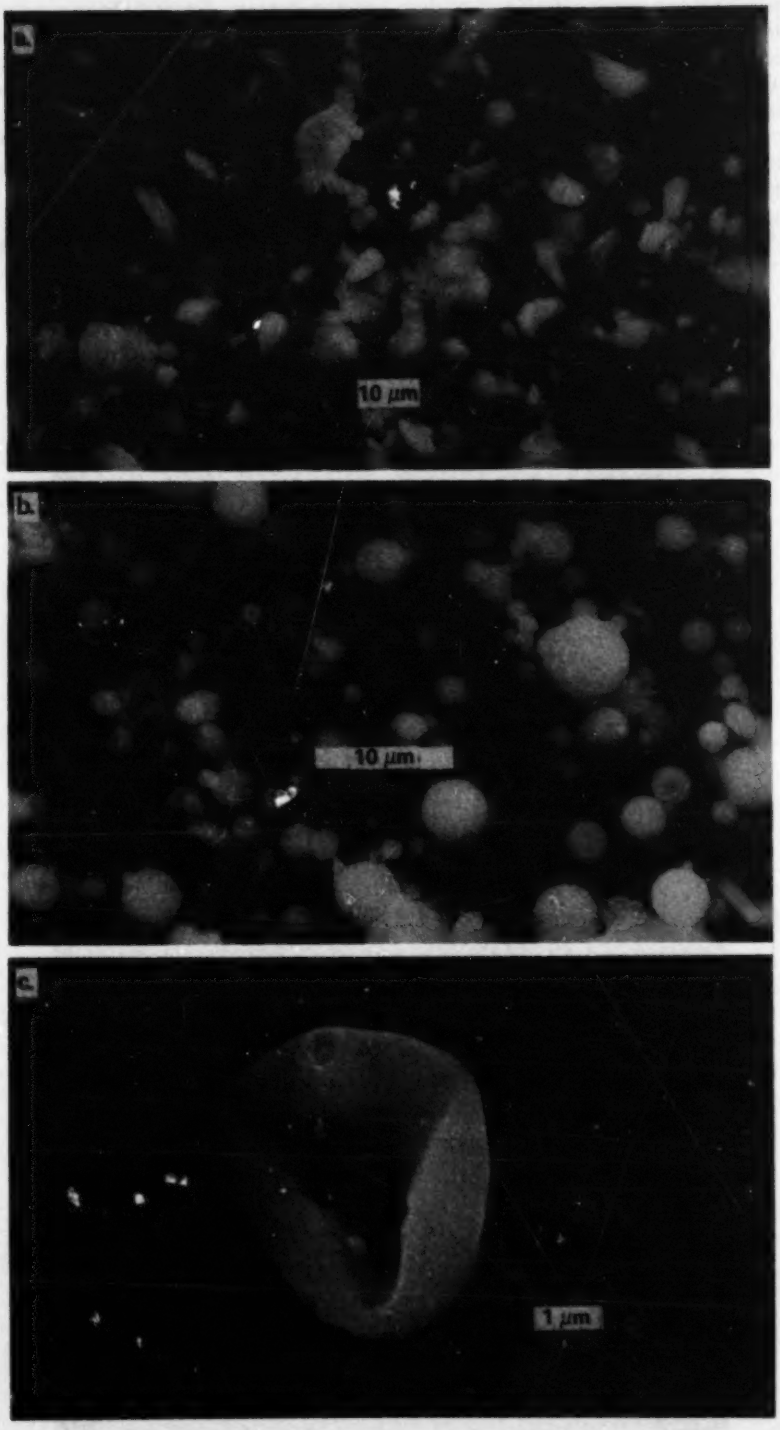

Fig. 2. Micrographs of coarse particles representing (a) resuspended soil from downtown Philadelphia, (b) coal-fly ash emissions and (c) airborne spore at site 28.

illustrate the use of those criteria, Fig. 2 shows micrographs of coarse particle samples of (a) surface dust from downtown Philadelphia that was resuspended by an aerosol generator (Batterman *et al.*, 1988), (b) coal-fly ash emissions from a coal fired power plant in Philadelphia (Olmez *et al.*, 1989) and (c) a spore from ambient air at Site 28; Fig. 3 shows typical x-ray spectra. Both morphology and x-ray spectra are needed to distinguish among such particles. X-ray spectra can distinguish between carbonaceous and crustal particles (Fig. 3). Morphology can distinguish between fly ash and minerals within the crustal category and between botanical particles and soot within a carbon category. Figure 4 shows a micrograph with several coarse particle types indicated. Although oil-fired power plants in Philadelphia emitted spheres with major x-ray peaks similar to those of coal-fly ash, most oil-fly ash particles were emitted in the fine fraction (Olmez *et al.*, 1989). By using V and Ni as indicators , we detected only a negligible amount of oil-fly ash in ambient coarse particles.

Typical particle-count data are shown by size and category in Table 2, and component mass concentrations are shown in Tables 2 and 3. Mass concentra-

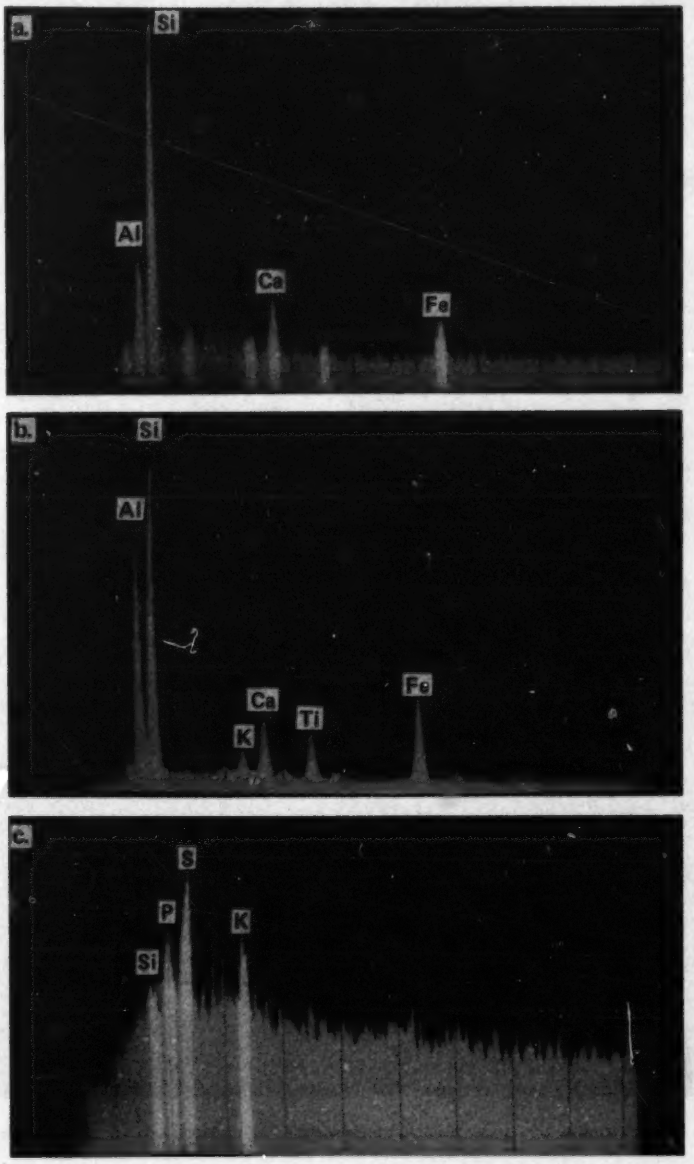

Fig. 3. X-ray spectra of (a) soil mineral, (b) coal-fly ash particle, and (c) spore.

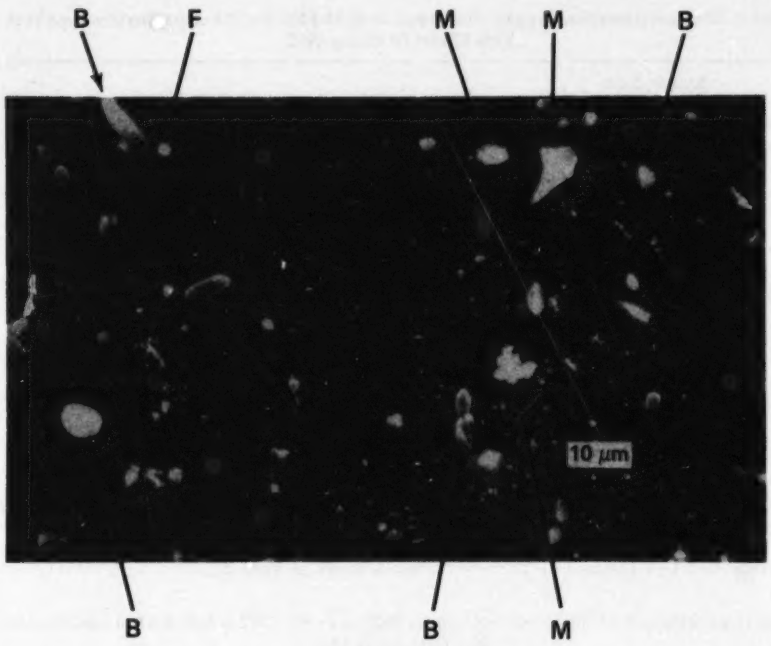

Fig. 4. Micrograph of atmospheric coarse particles collected at Site 28. Particle types are botanical (B), mineral (M) and coal-fly ash (F).

Table 2. Coarse particle count and estimated mass concentration by category at Camden, NJ, for 12-h periods beginning at 0600 and 1800 on 21 July 1982

	Category	Diameter range* ≤1.5	≤2.1	≤3.1	≤5.1	≤7.1	≤10	Mass ($\mu g\ m^{-3}$)
Day†								
	Mineral	1	15	26	29	10	6	7.7 ± 3.1
	Cl-rich mineral			1				0.01 ± 0.05
	Coal-fly ash		1		1			0.06 ± 0.06
	Botanical		11	23	33	6	2	2.3 ± 0.9
	Incinerator	1		3	1			0.1 ± 0.1
	Other	4	14	6	6			0.8 ± 0.3
Night‡								
	Mineral	1	36	38	30	8	1	8.5 ± 3.4
	Cl-rich mineral		2	2	6	1	1	2.1 ± 0.8
	Coal-fly ash	6	17	7	4			0.7 ± 0.3
	Botanical		4	11	9	4	1	2.0 ± 0.8
	Incinerator	3	13	10	10	1		1.8 ± 0.7
	Zn-rich			1		1		0.41 ± 0.2
	Other	6	6	10	8			0.9 ± 0.9

* For the sequence of size ranges shown, the effective diameters were < 1.5, 1.8, 2.55, 4.05, 6.3 and 8.8 μm.
† 200 particles were analyzed in a scanned area of 47,300 μm^2.
‡ 258 particles were analyzed in a scanned area of 90,000 μm^2.

tions were estimated for each class of particles from the following data: effective diameter for each size range, assumed density, fraction of filter area scanned, and air volume sampled. Accuracy estimates were based on uncertainties in density shown in Table 1, 40% uncertainty in estimating particle volume and counting statistics.

Minerals rich in Cl were detected only for the sampling period that began at 1800 on 21 July when the incinerator component had its largest value. We assume that the Cl-rich minerals were associated with incinerator emissions but did not know if they were emitted by incinerators or if they were the product of reactions between gas phase Cl from incinerators and minerals from other sources. Therefore, the Cl-rich minerals component shown in Table 2 was divided between the incinerator and mineral components as a footnote in Table 3 specifies.

Table 3. Mass concentrations in $\mu g\,m^{-3}$ estimated by SEM-EDX for 12-h coarse particle samples at Sites 12 and 28 during 1982

Sample start Date	Time	Botanical	Coal-fly ash	Mineral	Incinerator
Site 12					
5 August	1800	4.1 ± 1.6	0.00 ± 0.02	3.8 ± 1.5	*
6 August	0600	1.3 ± 0.5	0.16 ± 0.06	3.8 ± 1.5	*
6 August	1800	0.9 ± 0.4	0.10 ± 0.04	2.2 ± 0.9	0.0 ± 0.1
11 August	0600	1.5 ± 0.6	0.18 ± 0.07	1.6 ± 0.6	0.0 ± 0.1
11 August	1800	2.1 ± 0.8	0.08 ± 0.03	0.4 ± 0.1	0.0 ± 0.1
Site 28					
21 July	0600	2.3 ± 0.9	0.06 ± 0.04	7.7 ± 3.1	0.1 ± 0.1
21 July	1800	2.0 ± 0.8	0.74 ± 0.30	9.6 ± 3.6†	2.9 ± 1.3†
5 August	1800	4.0 ± 1.6	0.04 ± 0.02	5.3 ± 2.1	*
6 August	0600	1.0 ± 0.4	0.32 ± 0.13	5.8 ± 2.1	*
6 August	1800	0.4 ± 0.2	0.00 ± 0.02	2.9 ± 1.2	0.0 ± 0.1
11 August	0600	1.6 ± 0.6	0.15 ± 0.06	3.3 ± 1.3	0.6 ± 0.2
11 August	1800	0.5 ± 0.2	0.08 ± 0.03	1.1 ± 0.4	0.0 ± 0.1
Unweighted mean		1.8 ± 0.7	0.16 ± 0.06	4.0 ± 1.6	0.3 ± 0.2
Standard deviation		1.2	0.19	2.8	0.6

*Not analyzed by SEM-EDX.
†Includes 1.1 ± 1.1 $\mu g\,m^{-3}$ of the Cl-rich minerals shown in Table 2.

Table 4. Chemical mass balance for 12-h sample beginning at 0600 on 21 July 1982 at Site 28 when wind direction was $\theta = 13° \pm 22°$. Data are in $ng\,m^{-3}$

	Calculated	Obs	Soil	Flyash	Botanical	SO_4^{2-}	Incinerator	Vehicles	Sb roast
Al*	315 ± 134	319	249	11	0	0	52	2	0
Si*	1070 ± 344	1082	968	11	0	0	88	3	0
S*	89 ± 40	89	13	0	7	32	33	4	0
Cl	148 ± 32	34	1	0	0	0	144	3	0
K*	125 ± 22	123	58	1	19	0	46	1	0
Ca	177 ± 42	347	63	1	6	0	103	3	0
Ti	51 ± 12	34	39	1	0	0	10	0	0
Cr	5 ± 3	6	4	0	0	0	1	0	0
Mn	4 ± 2	7	3	0	0	0	1	0	0
Fe	265 ± 42	341	239	5	1	0	17	3	0
Ni	3 ± 1	2	1	0	0	0	1	0	0
Zn*	47 ± 38	49	2	0	0	0	44	1	0
Br	8 ± 3	8	0	0	0	0	1	6	0
Cd*	1 ± 2	1	0	0	0	0	1	0	0
Sb*	−1 ± 3	−1	0	0	0	0	0	0	−1
Pb*	39 ± 9	39	2	0	0	0	17	19	0
Botan*	2254 ± 800	2270	0	0	2254	0	0	0	0
F-ash*	60 ± 30	60	0	60	0	0	0	0	0
Mass	7434 ± 2866	9445	3712	60	2254	95	1026	288	−1
δmass	1536	2768	1164	30	790	127	571	197	4

*Species included in least squares fit.

Chemical mass balance results

SEM-EDX results for fly ash and botanical particles were included with XRF data in CMB calculations in which the concentration C_i of species i is

$$C_i = \sum A_{ij} M_j, \quad (1)$$

where A_{ij} is the abundance of species i in component j, and M_j is the total mass concentration for component j. Using data on A_{ij}, unknown values M_j were found by a least-squares method that minimizes the expression,

$$\chi^2 = \sum (C_i - O_i)^2 / E_i^2 \quad (2)$$

where O_i is the observed concentration of species i, and E_i^2 is the effective variance, which includes uncertainties in O_i and A_{ij} (Watson *et al.*, 1984). For a species i to be included in Equation (2), two criteria must be met:

(a) all sources of the species must be included in Equation (1), and
(b) the species' abundance A_{ij} must be known for all of those sources.

Tables 4 and 5 indicate the species and sources included in our CMB as well as typical CMB results. The soil signature represents an average for the Philadelphia area (Batterman *et al.*, 1988). Signatures for

Table 5. Chemical mass balance for 12-h sample beginning at 1800 on 21 July 1982 at Site 28 when wind direction was $\theta = 318° \pm 20°$. Data are in ng m^{-3}

	Calculated	Obs	Soil	Flyash	Botanical	SO_4^{2-}	Incinerator	Vehicles	Sb roast
Al*	700 ± 262	747	390	142	0	0	162	7	0
Si*	1939 ± 581	1903	1515	138	0	0	273	13	0
S*	178 ± 79	178	20	4	6	28	102	17	0
Cl	459 ± 106	244	2	1	0	0	445	11	0
K*	263 ± 56	260	90	10	17	0	143	4	0
Ca	453 ± 83	485	99	17	5		318	14	0
Ti	106 ± 17	67	62	10	0	0	32	2	0
Cr	9 ± 4	9	6	0	0	0	3	0	0
Mn	9 ± 3	16	4	0	0	0	3	2	0
Fe	502 ± 66	513	373	60	0	0	54	14	0
Ni	6 ± 2	2	2	0	0	0	3	0	0
Zn*	143 ± 119	154	3	0	0	0	137	2	0
Br	29 ± 13	25	0	0	0	0	4	25	0
Cd*	3 ± 3	3	0	0	0	0	3	0	0
Sb*	7 ± 4	7	0	0	0	0	1	0	6
Pb*	134 ± 33	134	3	0	0	0	54	76	0
Botan*	1945 ± 700	1950	0	0	1945	0	0	0	0
F-ash*	746 ± 250	740	0	746	0	0	0	0	0
Mass	12,911 ± 2842	14,736	5808	746	1945	85	3179	1139	8
δmass	2707	2768	2148	248	699	257	1318	598	5

*Species included in least squares fit.

stationary source emissions were from Olmez *et al.* (1989). The composition of pollen (Stanley and Linskens, 1974) was assumed to represent botanical particles. In Tables 4 and 5, the 'calculated' uncertainties are E_i, and δmass is the uncertainty in mass derived in the least squares analysis. (Any investigator may obtain the source signatures, ambient data and CMB code on a 360 kbyte IBM-PC readable diskette by sending such a diskette to the principal author.)

To determine if SEM data were essential for determining botanical matter and coal-fly ash, CMB analyses were made using only XRF data. Uncertainties increased by factors of 9 for botanical matter and 20 for coal-fly ash, and those components were undetectable.

CMB computations were made for each of 12 samples using the sources and fitting species listed in Table 4. Figure 5 compares CMB results for soil with SEM-EDX results for minerals. The former are based mainly on XRF data for Al and Si whereas the latter are based only on SEM-EDX data. There is agreement within the estimated uncertainties, which suggests that both methods are equivalent for soil and minerals. Thus, there was no need to include SEM data for minerals in the CMBs.

Figure 6 compares CMB and SEM-EDX results for incinerator emissions. In several cases CMB results are significantly higher than SEM-EDX results. To find the cause of the discrepancies, we examined the mass balances for two cases. Table 5 shows a case for Site 28 when the wind direction was 318 ± 20°, and site 28 was directly downwind of two large municipal incinerators. Then, the incinerator component had its largest value, and SEM-EDX and CMB results shown in Tables 3 and 5, respectively, were in good agreement.

Table 4 shows a case when the CMB result was 1.0 ± 0.6 μg m^{-3}, yet the SEM-EDX result was only 0.1 ± 0.1 μg m^{-3} (Table 3). The wind direction was 13 ± 22°, and Fig. 1 shows no upwind incinerator. The discrepancy could be due either to negative bias for SEM-EDX or positive bias for CMB. Negative bias would occur for SEM-EDX determinations if Cl, an important element, were volatilized from incinerator particles during transport from sources beyond the region shown in Fig. 1. Although incinerator particles are distinguished from soil minerals by Cl and Zn peaks in their EDX spectra (Mamane, 1988), loss of Cl during transport could cause some incinerator particles to be wrongly identified as soil minerals. Rapid loss of Cl was noted for *fine* incinerator particles transported only a short distance (Dzubay *et al.*, 1988; Dzubay, 1988). Less rapid, but still significant loss of Cl is expected for coarse particles. Positive bias in CMB results can be explained as follows: Abundant elements in the incinerator component are K, Zn and Cd, but Cd was below its detection limit, which means that the CMB results were effectively determined by K and Zn. Because we used a CMB model in which incinerators were the *only* significant sources of Zn, any Zn from other sources will cause positive bias for CMB-based estimates of incinerator emissions.

Mass apportionment

We applied CMB analysis to data for each sampling period listed in Table 3, and the averages are shown in Table 6. Coarse particle CMBs were performed as illustrated in Tables 4 and 5. Fine particle CMBs were

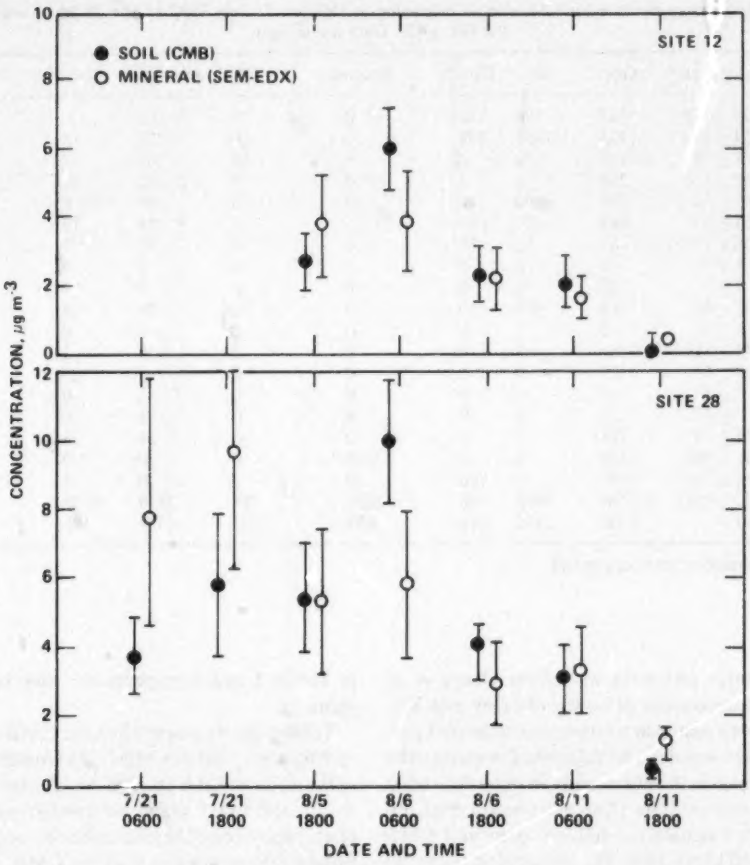

Fig. 5. Comparison of SEM-EDX results for minerals and CMB results for soil in the coarse fraction. CMB computations were made as in Tables 4 and 5.

Table 6. Average chemical mass balance results in $\mu g\ m^{-3}$ based on XRF, INAA, and SEM-EDX analyses of the 12 samples listed in Table 3*†

	Fine	Coarse	PM10
Sulfate and related ions	11.1 ± 1.2	0.3 ± 0.3	11.4 ± 1.2
Motor vehicle exhaust	2.4 ± 0.7	0.5 ± 0.2	2.9 ± 0.7
Soil	0.6 ± 0.1	3.8 ± 1.0	4.4 ± 1.0
Coal-fly ash	‡	0.16 ± 0.06	0.2 ± 0.1
Oil-fired power plants	0.4 ± 0.1	‡	0.4 ± 0.1
Ti-rich paint pigment	0.06 ± 0.04	‡	0.1 ± 0.1
Fluidized catalytic cracker	0.05 ± 0.05	‡	0.1 ± 0.1
Municipal incinerators§	1.4 ± 0.1	0.8 ± 0.4	2.2 ± 0.4
Antimony roaster	0.00 ± 0.01	0.01 ± 0.01	0.01 ± 0.01
Botanical matter (spores)	‡	1.7 ± 0.6	1.7 ± 0.6
Calculated total	16.0 ± 1.5	7.3 ± 1.4	23.3 ± 2.1
Measured total	15.2 ± 3.1	6.7 ± 2.8	21.9 ± 4.2

* Because the samples were not randomly chosen, the averages do not represent a particular season.
† XRF and INAA were applied to fine particles; XRF and SEM-EDX were applied to coarse particles.
‡ Not determined.
§ As explained in the text, results shown here represent an upper limit for incinerator emissions.

similar to those described previously (Dzubay *et al.*, 1988) except that crustal matter was represented by a signature for soil rather than dust. As a consequence of bias described above, our results for incinerators are upper limits.

Sums for the fine and coarse fractions are presented

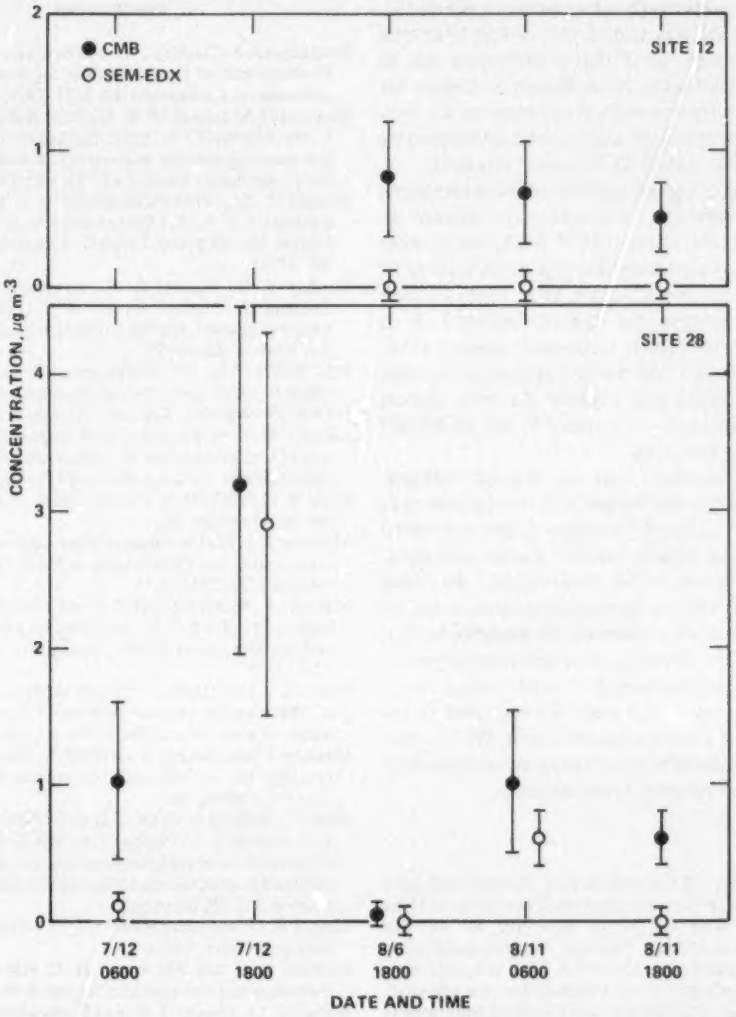

Fig. 6. Comparison of CMB and SEM-EDX results for incinerator emissions in the coarse fraction. CMB computations were made as in Tables 4 and 5.

as PM-10 results in Table 6. Although coal-fly ash and botanical matter were determined only for the coarse fraction, the fine fractions of those components is expected to be relatively small (Olmez *et al.*, 1989, Kapp, 1969), and little mass was missed by not applying SEM to fine particles. Likewise, emissions from oil-fired power plants and fluidized crackers were determined only in the fine fraction, but coarse particle emissions from such sources were relatively small at the source (Olmez *et al.*, 1989). Because samples were not chosen randomly, the average PM-10 mass concentration shown in Table 6 does not represent a particular season and is, in fact, 40% lower than the average for all samples collected between 14 July and 13 August 1982.

Additional CMB analyses were made with a coarse particle marine component included. On 6 August, when winds were from the east, the magnitude of this component was 1.6 and 3.5 $\mu g\,m^{-3}$ at Sites 12 and 28, respectively. The average for all sites and samples was $0.3 \pm 0.2\ \mu g\,m^{-3}$. This component was determined mainly by Cl, a volatilizable element, that caused overall accuracy to be poor (Dzubay, 1988).

CONCLUSIONS

By supplementing x-ray fluorescence data with microscopy data in our mass balance we were able to determine two additional components: coal-fly ash and botanical matter. Botanical matter contributed

8% to PM-10, and coal-fly ash contributed nearly 1%. While coal-fly ash was a small part of PM-10 at sites we studied, knowledge of that contribution can be valuable in developing cost-effective strategies for meeting air quality standards at any location. Coal-fly ash and botanical matter could not be determined by XRF data alone, and SEM data were essential.

For an event of known high impact from municipal incinerators, there was good agreement between results obtained by CMB and SEM-EDX, but at other times there were significant discrepancies. Loss of Cl during transport, would cause SEM-EDX to have negative bias because that method depended on Cl along with Zn to identify incinerator emissions. On the other hand, the CMB method applied to our data could have positive bias because Zn from sources other than incinerators was treated by our model as if it were from incinerators.

Samples in our study were not selected randomly but were selected to give insight into the application of SEM and CMB. Thus, the averages do not represent a particular season. Ideally, in future studies all samples would be analyzed by all methods, but the much higher cost of electron microscopy analysis suggests that only a subset of samples can be analyzed by that method. Random selection of samples would enable the subset to be representative of the entire population. Use of automated devices for control of the scanning electron microscope (Johnson, 1983; Casuccio *et al.*, 1983) could improve the speed and precision of analyses that we performed manually.

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